IV.B.8 Development of Novel Water-Gas-Shift Membrane Reactor

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Objectives

- Produce a reformate with <10 ppm CO at the high pressure used for reforming.
- Develop the water-gas-shift (WGS) membrane reactor for achieving <10 ppm CO.
- Verify the mathematical model developed to predict the performance of the WGS membrane reactor.
- Synthesize and characterize CO_2-selective membranes for the novel WGS membrane reactor.

Technical Barrier

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- Synthesize and characterize CO_2-selective membranes containing amino groups.
- Use the mathematical model developed to study membrane reactor performance and to guide/minimize experimental work.
- Use the CO_2-selective membrane synthesized to remove CO_2 for H_2 enhancement and decrease CO to <10 ppm.
- Drive the WGS reaction to the product side via CO_2 removal:

$$CO + H_2O \rightarrow H_2 + CO_2\uparrow$$

- Decrease CO to <10 ppm in the H_2 product via CO_2 removal.

Accomplishments

- Obtained <10 ppm CO in the reformate from initial WGS membrane reactor experiments using the small circular laboratory membrane cell ("Small Cell") with the synthesis gas feed with 1% CO. Confirmed the <10 ppm CO result using the "Big Cell" WGS membrane reactor in the rectangular flat-sheet shape with well-defined flow that had 7.5 times the membrane area of "Small Cell". This achieved the project milestone of <10 ppm CO in the H_2 product.
- The data from the "Big Cell" WGS membrane reactor agreed well with predictions from the mathematical model developed.

- Removed CO_2 from a syngas containing 17% CO_2 to about 30 ppm. The CO_2 removal data were in line with predictions of the mathematical model. The treated syngas with such a low CO_2 concentration can be readily processed to convert the carbon oxides to methane via methanation.
- Synthesized membranes with high CO_2 permeabilities and high CO_2/H_2 and CO_2/CO selectivities.

Future Directions

- Continue to synthesize and characterize improved membranes for the reactor.
- Complete the WGS membrane reactor demonstration.
- Investigate membrane stability.

Introduction

A water-gas-shift (WGS) reactor for the conversion of carbon monoxide (CO) and water to hydrogen (H_2) and carbon dioxide (CO_2) is widely used in chemical and petroleum industries. The reactor is also critically needed for gas clean up following the conversion of fuels, including gasoline, diesel, methanol, ethanol, natural gas, biomass, and coal, to H_2 for fuel cells. Since the WGS reaction is reversible, it is not efficient, resulting in a high concentration of unconverted CO (~ 1%) in the H_2 product and a bulky, heavy reactor. This reaction can be enhanced significantly through a CO_2-selective membrane, which removes the reaction product, CO_2, to beat the reaction equilibrium and shifts the reaction towards the product side. The CO_2-selective WGS membrane reactor has advantages including (1) a high-purity H_2 product is recovered at high pressure (feed gas pressure) and (2) air can be used as the sweep gas to remove the permeate, CO_2, on the low-pressure side of the membrane to have a high driving force for the separation. These advantages are especially important for fuel cell vehicles. The first advantage eliminates the need for a compressor. With the second advantage, the high driving force created by the air sweep can result in low CO concentration and high H_2 purity and recovery.

We have synthesized novel CO_2-selective polymer membranes containing amino groups with high CO_2 permeabilities and high CO_2/H_2 and CO_2/CO selectivities. We have obtained <10 ppm CO in the H_2 product using two WGS membrane reactors of different sizes. In other words, we have achieved the project milestone of <10 ppm CO in the H_2 product. In addition, we removed CO_2 from a syngas containing 17% CO_2 to about 30 ppm. The treated syngas with such a low CO_2 concentration can be readily processed to convert the carbon oxides to methane via methanation.

Approach

We have synthesized novel CO_2-selective membranes with high CO_2 permeabilities and high CO_2/H_2 and CO_2/CO selectivities by incorporating amino groups in polymer networks. We have incorporated the synthesized membrane into the WGS membrane reactors to show CO reduction to 10 ppm or lower in the H_2 product in reactor experiments using the synthesis gas feed with 1% CO. We have verified the mathematical model developed [1, 2] for the prediction of the performance of the "Big Cell" WGS membrane reactor. In the model, the low-temperature WGS reaction kinetics for the commercial catalyst (Cu/ZnO/Al_2O_3) reported by Moe [3] and others [4] was used. In addition, we have used the membrane to remove CO_2 from syngas for H_2 purification.

Results

Laboratory Membrane Reactor ("Small Cell") Experiments

During this year, we studied and conducted the WGS experiments using a laboratory WGS membrane reactor ("Small Cell", a circular cell) with the synthesis gas feed containing 1% CO (from autothermal reforming). The rationales for this CO level are two-fold: (1) it can be readily produced from commercial WGS reactors and (2) it requires CO_2 removal for its reduction via WGS reaction. In the membrane reactor experiments, the commercial Cu/ZnO catalyst supported on alumina was placed on the top of the membrane. The catalyst was activated/conditioned at 150°C and 2.1 atm first with the gas of

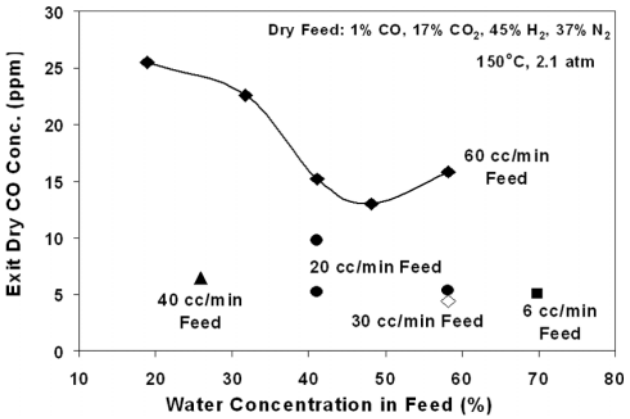

Figure 1. CO in the Reformate from the Laboratory Water-Gas-Shift Membrane Reactor ("Small Cell") with 1% CO Feed Gas at Various Flow Rates

1% H_2, 3% CO_2, 3% N_2, and 93% He for 6.1 hours and then with the gas of 40% H_2, 20% CO_2, and 40% N_2 until the CO concentration reached about 80 ppm (about 7.5 hours).

After the catalyst activation, the synthesis gas feed containing 1% CO, 17% CO_2, 45% H_2, 37% N_2 (on the dry basis) was admitted into the membrane reactor. The operating temperature was 150°C, and the feed pressure of the synthesis gas was 2.1 atm. Figure 1 summarizes all data obtained from this laboratory WGS membrane reactor ("Small Cell"). As shown in this figure, the CO concentration in the exit stream, i.e., the H_2 product, was <10 ppm (on the dry basis) for the various feed flow rates of the syngas at 6, 20, 30 and 40 cc/min under various feed water concentrations ranging from 15% to 70%. Even at a feed rate of 60 cc/min, the CO concentration in the exit stream was very close to 10 ppm at the feed water concentration of about 45%.

"Big Cell" Membrane Reactor Experiments

We constructed and set up a "Big Cell" membrane reactor for the task on the set-up and scale-up of a WGS membrane reactor. The "Big Cell" membrane reactor is a rectangular cell with a well-defined gas flow and velocity both for the feed and sweep sides. Thus, this membrane reactor is suitable for modeling and scale-up work. That is, the data from this membrane reactor can be used for comparison with modeling results and for scale-up.

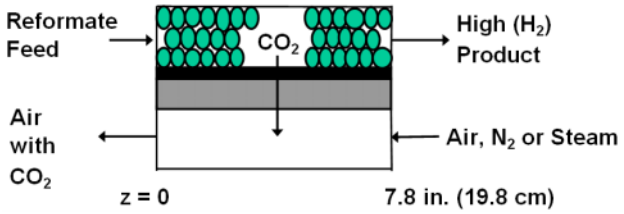

Figure 2. Schematic of the Rectangular "Big Cell" Water-Gas-Shift Membrane Reactor

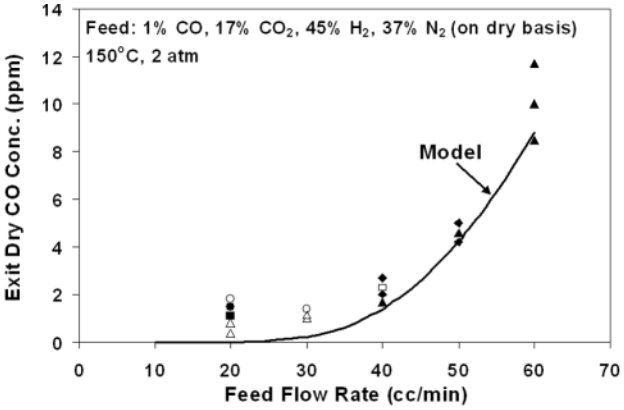

Figure 3. CO in the H_2 Product from the "Big Cell" Water-Gas-Shift Membrane Reactor with 1% CO Feed Gas at Various Flow Rates (each symbol represents a different series of experiments)

Figure 2 shows the schematic of this membrane reactor. This membrane reactor has 7.5 times the membrane area of the laboratory membrane reactor ("Small Cell").

In the membrane reactor experiments using the "Big Cell", the catalyst activation was conducted similarly to that described earlier for the "Small Cell" membrane reactor. After the catalyst activation, the synthesis gas feed containing 1% CO, 17% CO_2, 45% H_2, 37% N_2 (on the dry basis) entered into the membrane reactor. The operating temperature was 150°C, and the feed pressure of the synthesis gas was 2 atm. Figure 3 shows the results obtained from this "Big Cell" WGS membrane reactor. As shown in this figure, the CO concentration in the exit stream, i.e., the reformate, was <10 ppm (on the dry basis) for the various feed flow rates of the syngas at 20, 30, 40, 50, and 60 cc/min. The data agreed reasonably with the prediction by the non-isothermal mathematical model that we have developed [1, 2] based on the material and energy balances,

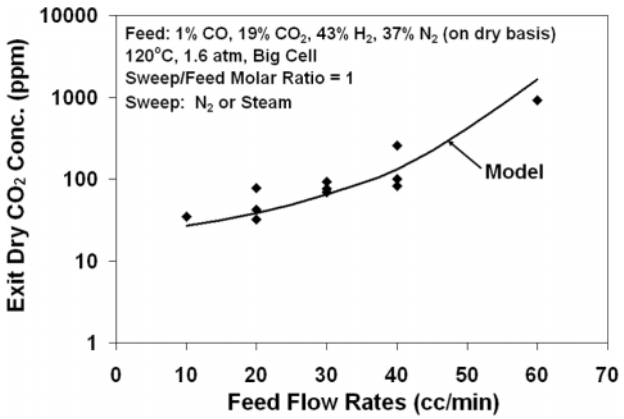

Figure 4. CO_2 Concentration in the Exit Stream (the H_2 product) from the "Big Cell" (without catalyst particles) for the Syngas Feed with 1% CO and 17% CO_2 at Various Flow Rates

membrane permeation, and the low-temperature WGS reaction kinetics for the commercial catalyst ($Cu/ZnO/Al_2O_3$) reported by Moe [3] and others [4].

Effective Removal of CO_2 from Syngas

The "Big Cell" without the catalyst particles was used for the removal of CO_2 from the same syngas (1% CO, 17% CO_2, 45% H_2, 37% N_2 (on the dry basis)). The membrane we synthesized was also used for the removal of CO_2 from this syngas using nitrogen as the sweep gas at the sweep/feed molar ratio of 1. Figure 4 depicts the resulting CO_2 concentrations (on the dry basis) in the exit stream (the H_2 product) at 120°C and 2 atm from the rectangular membrane cell at various feed flow rates. As depicted in this figure, a low CO_2 concentration of about 30 ppm was obtained for a feed flow rate of about 20 cc/min, indicating a nearly complete removal of CO_2 from the syngas. Even at the high feed rate of 60 cc/min, the CO_2 concentration in the exit stream was less than 1000 ppm (0.1%). Using steam instead of nitrogen as the sweep gas also gave similar, good results. Figure 4 shows that the data are in good agreement with the model that we have developed [1, 2] based on the material and energy balances and membrane permeation.

Conclusions

We have synthesized novel CO_2-selective polymer membranes containing amino groups with high CO_2 permeabilities and high CO_2/H_2 and CO_2/CO selectivities. We have obtained <10 ppm CO in the H_2 product in initial WGS membrane reactor experiments using the small circular laboratory membrane cell ("Small Cell") with the synthesis gas feed with 1% CO. We have confirmed the <10 ppm CO result using the "Big Cell" reactor with well-defined flow, which has a WGS membrane 7.5 times the area of "Small Cell". In other words, we have achieved the project milestone of <10 ppm CO in the H_2 product. The data from the "Big Cell" WGS membrane reactor agreed well with the mathematical model developed, which can be used for scale-up. In addition, we removed CO_2 from a syngas containing 17% CO_2, achieving about 30 ppm. The CO_2 removal data were consistent with predictions from the mathematical model developed.

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2. J. Huang and W. S. W. Ho, "A Modeling Study of CO_2-Selective Water-Gas-Shift Membrane Reactor for Fuel Cell", Proceedings of the Topical Conference on Advanced Membrane-Based Separations at AIChE Annual Meeting, San Francisco, CA, Paper 171c (2003).

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2. J. Zou, G. Shil, and W. S. W. Ho, "Carbon Dioxide-Selective Membranes for Hydrogen Purification and Gas Separation", Proceedings of the Topical Conference on Advanced Membrane-Based Separations at AIChE Annual Meeting, San Francisco, CA, Paper 74t (2003).

3. J. Huang and W. S. W. Ho, "A Modeling Study of CO_2-Selective Water-Gas-Shift Membrane Reactor for Fuel Cell", Proceedings of the Topical Conference on Advanced Membrane-Based Separations at AIChE Annual Meeting, San Francisco, CA, Paper 171c (2003).

4. W. S. W. Ho, "Facilitated Transport Membranes for Environmental and Energy Applications", Industrial Technology Research Institute, Energy & Resources Laboratories, Hsinchu, Taiwan, December 16, 2003.

5. W. S. W. Ho, "Facilitated Transport Membranes for Environmental and Energy Applications", Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, December 17, 2003.

6. W. S. W. Ho, "Fuel Cell and Membrane Technology: An Overview", Departments of Chemistry and Physics, Soochow University, Taipei, Taiwan, December 18, 2003.

7. W. S. W. Ho, "Facilitated Transport Membranes for Environmental and Energy Applications", Department of Chemical Engineering, Chung-Yuan University, Chung-Li, Taiwan, December 19, 2003.

8. W. S. W. Ho, "Engineering Membranes for Environmental and Energy Applications", HydrogenSource LLC, South Windsor, CT, February 25, 2004.

Patent Application Filed

1. W. S. Winston Ho, "CO_2-Selective Membranes Containing Amino Groups", U. S. Patent Application Serial No. 10/145,297, filed on May 14, 2002.